



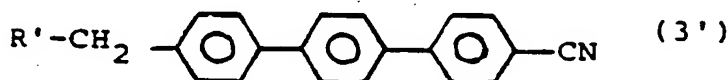
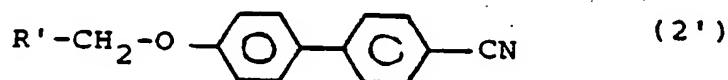
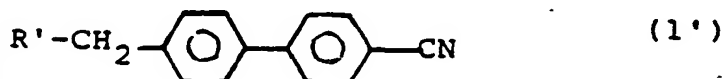
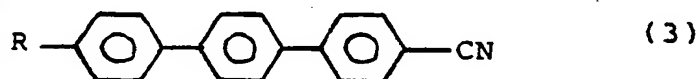
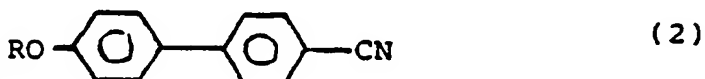
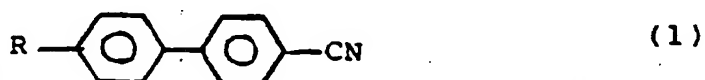
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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## (54) Title: SMECTIC A LIQUID CRYSTAL COMPOSITIONS

## (57) Abstract

Liquid crystal compositions comprising as a first part between 40 and 99% by weight in aggregate of one or more materials selected from one or more of the six compound classes (1) to (3'), wherein R is in every instance an alkyl chain containing between 2 and 18 carbon atoms and R' is in every instance an alkyl chain containing between 1 and 17 carbon atoms, wherein one or more non-adjacent CH<sub>2</sub>-groups are replaced by oxygen atoms, and as a second part between 1 and 60% by weight of one or more materials of high birefringence and high positive dielectric anisotropy which raise the S<sub>A</sub>-N transition temperature, exhibit a smectic A phase of relatively low melting point and wide smectic range. Such compositions may be used in liquid crystal cells, not only in display or optical information processing applications, but also for instance in temperature sensing applications. The operation of such cells may involve laser addressing, thermal or electrical addressing.



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SMECTIC A LIQUID CRYSTAL COMPOSITIONS

The present invention relates to liquid crystal compositions which exhibit a smectic A phase of relatively low melting point and wide smectic range.

5 Such compositions may be used in liquid crystal cells, not only in display or optical information processing applications, but also for instance in temperature sensing applications. The operation of such cells may involve laser addressing, thermal or electrical  
10 addressing.

Smectic A liquid crystals are highly viscous and therefore often require substantially greater energy, in the form of heat, light or electric field, to effect any molecular change in the phase than do typical nematic or  
15 cholesteric liquid crystals.

From a practical point of view, for most applications, it is desirable for the smectic A phase to exist at room temperature. It is also desirable for this smectic A phase to be present over a relatively wide  
20 temperature range in order that it may be used, without recourse to thermostating, in equipment that is designed for use in situations involving a wide range of service temperature. Typical smectic A mixtures that are currently commercially available exhibit somewhat  
25 inconveniently narrow ranges of smectic A phase for a number of applications. Thus it is seen from the following table of smectic A phase materials commercially available from BDH Chemicals Ltd. under the designations

S1 to S5 that the lower end of the service temperature range does not extend significantly below the freezing point of water, while the upper end is limited to between about 40 and 55°C.

		K-S <sub>A</sub>	S <sub>A</sub> -N	N-I
5	S1	5	40	43°C
	S2	-1	48	49
	S3	0	55	61
	S4	0	54	57
10	S5	1	55.5	61

An object of the present invention is the provision of liquid crystal mixtures with an extended temperature range for the smectic A phase, typically one that extends to cover the range from about -10°C to about +70°C, but the scope of the invention is not restricted to this temperature range.

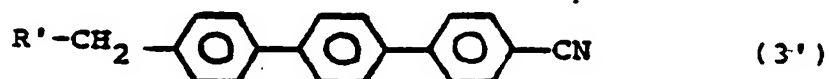
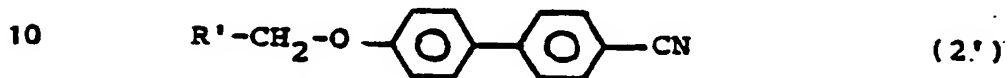
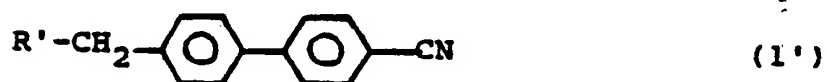
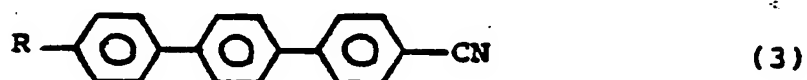
It should be noted that, to be useful in the types of smectic A displays described above, the smectic A liquid crystal mixtures must also possess other appropriate properties in addition merely to the smectic A phase. For example, many of the display principles involved depend upon reorienting the liquid crystal to a homeotropic state by means of an external electric field to erase information written on the display. This reorientation may be performed in the smectic phase, in the nematic phase, or in the isotropic phase just above the N-I transition where sufficient post-translational order remains. So that this reorientation may be achieved by the minimal electric field (i.e. the minimum applied voltage) it is desirable that the smectic A components possess a relatively high positive dielectric anisotropy. Furthermore, many of the types of smectic displays described above depend for their optical contrast on a difference in texture between the part upon which information is written and the part upon which information is not written. Various means are adopted according to the display technology to induce a light

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scattering texture in the part where information is written. The efficacy of the scattering process towards incident light of visible wavelengths depends upon the optical birefringence of the smectic liquid crystal, and this, therefore, preferably should also be relatively high. Furthermore, an attractive feature of the smectic A type of display depends upon the fact that the scattering texture so induced is permanent so that information written into the display does not need to be refreshed continuously as in the twisted nematic or phase-change types of display, thus simplifying the electronic driving circuits. Now experience has shown that the stability of the scattering texture does not persist throughout the whole of the  $S_A$  phase but diminishes with increasing temperature of the display because at a particular temperature the scattering texture is reoriented from the surrounding unwritten homeotropic part, thus spontaneously erasing the written information. It is important that the temperature at which reorientation occurs be well above any temperature that the display will experience. In general this temperature is proportional to the  $S_A$ -N transition temperature of the mixture. Finally of course, the additives incorporated for the purpose of raising the  $S_A$ -N transition temperature must be stable optically and thermally, and must not suffer electrochemical degradation under the voltages necessary to operate the display. It is an object of this invention to provide additives with the properties described above.

These compositions may be used as they are, or they may form a base mixture to which may be added up to 10% by weight in aggregate of one or more chiral, ionic, surfactant, and/or guest dye and the like additions.

According to the present invention there is provided a liquid crystal composition exhibiting a smectic A phase comprising as a first part between 40 and 99 % by weight in aggregate of one or more materials selected from one or more of the following six compound classes,



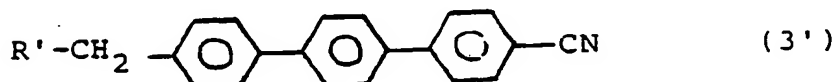
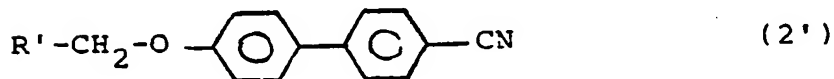
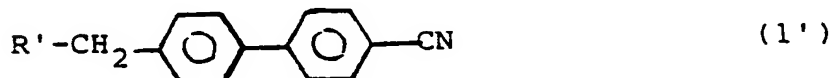
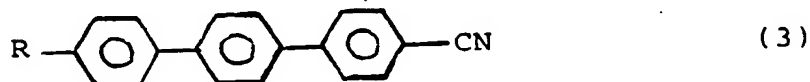
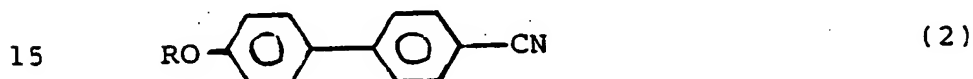
wherein R is in every instance an alkyl chain containing between 2 and 18 carbon atoms and R' is in every instance an alkyl chain containing between 1 and 17 carbon atoms, wherein one or more non-adjacent CH<sub>2</sub>-groups are replaced by oxygen atoms,

and as a second part between 1 and 60 % by weight of one or more materials of high birefringence and high positive dielectric anisotropy which raise the S<sub>A</sub>-N transition temperature.

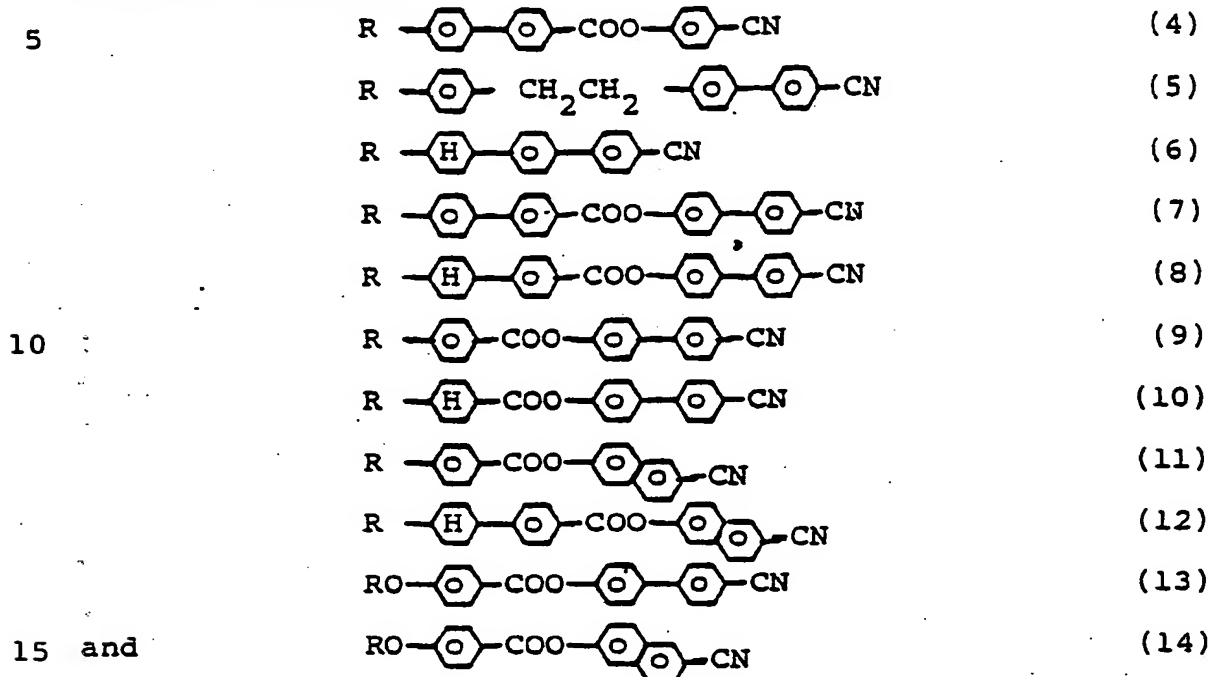
20 Preferably the second part material comprises between 3 and 60 %, in particular between 10 and 30 % by weight of the liquid crystal composition. The second part materials are of high birefringence, i.e.  $\Delta n > 0,15$ , in particular  $> 0,17$ . The dielectric anisotropy of the second part materials is  $> + 8$ , in particular  $> + 10$ . Preferably the second part materials are compounds comprising three or four ring structures. They preferably contain at least two 1,4-phenylene rings preferably a

4-cyanobiphenyl-4'-yl group, a bridging element selected from the group consisting of -O-CO-, -CO-O- and -CH<sub>2</sub>CH<sub>2</sub>- and/or one trans-1,4-cyclohexylene ring.

According to the present invention there is  
5 provided a liquid crystal composition exhibiting a smectic A phase, which composition either consists exclusively of a base mixture or consists of a base mixture together with not more than 10% by weight in aggregate of one or more other constituents,  
10 characterised in that the base mixture contains, as a first part, between 40 and 99% by weight in aggregate of one or more materials selected from one or more of the following six compounds classes,



and in that the balance of the base mixture is provided by a second part consisting of one or more materials selected from one or more of the following eleven compound classes,



wherein R is in every instance an alkyl chain containing between 2 and 18 carbon atoms, and R' is in every instance an alkyl chain containing between 1 and 17 carbon atoms, wherein one or more non-adjacent CH<sub>2</sub>-groups are replaced by oxygen atoms.

The compound classes (1) and (2) of the first part of the mixture, where R is a straight chain alkyl group containing more than 7 carbon atoms, are known smectic A phase liquid crystals, some of which have an S<sub>A</sub> phase in the vicinity of room temperature. Thus, the n-octyl homologue of compound of class (1), 4-cyano-



4'-n-octyl biphenyl, has the transition temperatures  $K-S_A$ ,  $21.5^{\circ}\text{C}$ ;  $S_A-N$ ,  $33.5^{\circ}\text{C}$ ;  $N-I$ ,  $40.5^{\circ}\text{C}$ . The temperature range of the smectic phase can be extended somewhat by mixing two or more homologues. Thus a mixture of 58% of the n-octyl homologue with 42% of the n-decyl has the constants  $K-S_A$ ,  $5^{\circ}\text{C}$ ;  $S_A-N$ ,  $40^{\circ}\text{C}$ ;  $N-I$ ,  $43^{\circ}\text{C}$ . However, the relatively low transition temperatures of compounds of class (1) preclude the possibility of preparing a mixture suitable for most practical displays from these components alone.

Compounds of class (2), where R is a straight chain alkyl group containing more than 7 carbon atoms, have higher  $S_A-N$  transition temperatures, typically about  $70^{\circ}\text{C}$ , but their melting points are also much higher, typically  $50-60^{\circ}\text{C}$ . Mixtures composed only of compounds of class (2) can be prepared with  $S_A-N$  transition temperatures approaching  $70^{\circ}\text{C}$ , but their melting points are typically in the range  $30$  to  $40^{\circ}\text{C}$ , rendering them unsuitable for use in displays operating at ambient temperatures. Compounds of class (2) are nonetheless useful when mixed with compounds of class (1) in depressing the freezing point. Thus a mixture of 50% of the n-octyl homologue of class (1) with 38% of the n-decyl homologue of class (1) and 12% of the n-decyl homologue of class (2) has the transition temperatures  $K-S_A$ ,  $-1^{\circ}\text{C}$ ;  $S_A-N$ ,  $48^{\circ}\text{C}$ ;  $N-I$ ,  $49^{\circ}\text{C}$ .

Compounds of class (3) enable the  $S_A$  phase of mixtures with classes (1) and (2) to be extended a little further, but their solubility in these mixtures is limited and the melting points soon become unacceptably high if too much is used.

The desirable dielectric, optical and stability properties of the additive(s) forming the second part of the mixture have been described above, and these properties are exhibited by additives of classes (4) to (14). As far as the thermotropic properties are concerned it is desirable that the additive(s) exhibit an

$S_A$  phase stable up to as high a temperature as possible. Such phases are exhibited by the higher homologues of all the compounds of classes (4) - (14). However, occurrence of an enantiotropic  $S_A$  phase in the additive is not obligatory as is evident from example (2), where the additive is from compound class (6), where  $R = C_5H_{11}$ , and example (6) where the additive is from compound class (10), where  $R = C_2H_5$ , in neither of which instances does the additive exhibit an enantiotropic  $S_A$  phase.

The elevating effect of a single additive of the second part of the base mixture on the transition temperatures of the first part is typically proportional to its concentration as exemplified below. The proportion of a single additive that can be used is limited by its solubility in the first part, too high a concentration also raising the melting point. Judicious choice of the concentration however, can result in a depression of the melting point, which is desirable. Some additives raise the N-I transition faster than the  $S_A$ -N; some have the reverse effect, thus enabling the width of the nematic range, which is an important characteristic in some types of smectic displays, to be controlled.

The elevating effects of more than one additive of the second part of the base mixture on the transition temperature of the first part are cumulative as shown by examples (15) to (22) below. The use of more than one additive may be desirable since each exercises an incremental depression on the onset of melting. Moreover the more complex mixtures become increasingly difficult to freeze. Thus this invention provides smectic mixtures with a wide range of thermotropic properties.

The following description of specific examples of the invention illustrate its utility and how the temperature range of smectic A phases consisting of one or more members of compound classes (1) to (3) may be extended by addition of one or more members of compound classes (4) to (14).

Example 1 (use of a compound of class (5) )

5 A smectic mixture was formed with the following composition by weight :-

47.5%	4-cyano-4'- <u>n</u> -octylbiphenyl
37.05%	4-cyano-4'- <u>n</u> decylbiphenyl
10.45%	4-cyano-4'- <u>n</u> -decyloxybiphenyl
5.0%	4-cyano-4"- <u>n</u> -nonylterphenyl.

10 This mixture, hereinafter referred to as mixture A, has transition temperatures  $S_A-N$ ,  $54^{\circ}\text{C}$ :  $N-I$ ,  $56.2 - 59.4^{\circ}\text{C}$ .

15 Mixture A was mixed in different proportions by weight with 1-(4-cyano-4'-biphenyl)-2-(4-n-octylphenyl) ethane (compound 5.1), and the table records measured transition temperatures for those mixtures :

20	Mixture A	Compound 5.1	$S_A-N$ Transition temperature	$N-I$ Transition temperature
	95%	5%	$57.0^{\circ}$	$58.0-60.0^{\circ}$
	90%	10%	$60.5^{\circ}$	$61.0-63.5^{\circ}$
25	85%	15%		64-68 (S-I: no nematic phase)

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Example 2 (use of a compound of class (6) )

A smectic mixture was formed with the composition  
by weight :

58.8%	4-cyano-4'- <u>n</u> -octylbiphenyl
28.4%	4-cyano-4'- <u>n</u> decylbiphenyl
18.8%	4-cyano-4'- <u>n</u> -octyloxybiphenyl

This mixture, hereinafter referred to as mixture B, has  
transition temperatures  $S_A-N$ ,  $46.6^{\circ}\text{C}$ ;  $N-I$ ,  $50.8-51^{\circ}\text{C}$ .

Mixture B was mixed in different proportions by  
weight with 4-cyano-4'-(4-n-pentylcyclohexyl)-biphenyl  
(compound 6.1), and the table below records measured  
transition temperatures for those mixtures :

Mixture B	Compound 6.1	$S_A-N$ Transition temperature	$N-I$ Transition temperature
98%	2%	$48.1^{\circ}$	$53.5-53.7^{\circ}$
96%	4%	$49.5^{\circ}$	$55.8-56.3^{\circ}$
94%	6%	$50.8^{\circ}$	$58.0-58.8^{\circ}$
92%	8%	$51.9^{\circ}$	$59.9-60.9^{\circ}$

Example 3 (use of a compound of class (7) )

Mixture A was mixed in different proportions by  
weight with 4-cyano-4'-biphenyl 4-n-heptylbiphenyl-4'-  
carboxylate (compound 7.1), and the table below records  
measured transition temperatures for those mixtures :

5	Mixture A	Compound 7.1	S <sub>A</sub> -N Transition temperature	N-I Transition temperature
	99%	1%	55.7°	57.5-59.2°
	98%	2%	56.9°	58.8-61.6°
10	97%	3%	58.4°	60.2-64.0°
	96%	4%	59.7°	61.7-66.7°
	95%	5%	61.0°	62.8-69.1°

15 Example 4 (use of a compound of class (9) )

Mixture A was mixed in different proportions by weight with 4-cyano-4'-biphenyl 4-n-decylbenzoate (compound 9.1), and the table below records measured transition temperatures for those mixtures :

25	Mixture A	Compound 9.1	S <sub>A</sub> -N Transition temperature	N-I Transition temperature
	95%	5%	58.5°	60.3-62.3°
	90%	10%	63.8°	65.2-68.6°
30	85%	15%	69.3°	69.3-75.2°

Example 5 (use of a compound of class (9) )

35 Mixture A was mixed in different proportions by weight with 4-cyano-4'-biphenyl 4-n-dodecylbenzoate (compound 9.2), and the table below records measured transition temperatures for those mixtures :

5	Mixture A	Compound 9.2	S <sub>A</sub> -N Transition temperature	N-I Transition temperature
	97%	3%	56.7°	57.9-60.0°
	94%	6%	59.4°	60.5-63.4°
10	91%	9%	62.5°	63.4-66.9°

Example 6 (use of a compound of class (10) )

15 Mixture A was mixed in different proportions by weight with 4-cyano-4'-biphenyl trans-4-n-ethylcyclohexane-1-carboxylate (compound 10.1), and the table below records measured transition temperatures for those mixtures :

20	Mixture A	Compound 10.1	S <sub>A</sub> -N Transition temperature	N-I Transition temperature
	97%	3%	55.4°	58.8-60.0°
25	94%	6%	57.3°	61.9-63.4°
	91%	9%	59.1°	65.6-67.5°
	88%	12%	60.6°	69.0-71.2°
30	85%	15%	62.0°	73.2-75.5°

Example 7 (use of a compound of class (10) )

35 Mixture A was mixed in different proportions by weight with 4-cyano-4'-biphenyl trans-4-n-pentylcyclohexane-1-carboxylate (compound 10.2), and the table below records measured transition temperatures for those mixtures :

5	Mixture	Compound	S <sub>A</sub> -N Transition	N-I Transition
	A	10.2	temperature	temperature
	97%	3%	56.7°	59.0-61.1°
	94%	6%	58.5°	61.5-63.5°
10	91%	9%	60.8°	64.8-67.1°
	88%	12%	63.6°	68.6-71.8°
	85%	15%	65.8°	72.0-75.3°

15 Example 8 (use of a compound of class (10) )

Mixture A was mixed in different proportions by weight with 4-cyano-4'-biphenyl trans-4-n-heptylcyclohexane-1-carboxylate (compound 10.3), and the table below records measured transition temperatures for those mixtures :

25	Mixture	Compound	S <sub>A</sub> -N Transition	N-I Transition
	A	10.3	temperature	temperature
	95%	5%	59.4°	60.9-64.1°
	90%	10%	63.8°	66.1-69.8°
30	85%	15%	69.0°	72.5-71.1°
	80%	20%	74.8°	79.5-84.6°

Example 9 (use of a compound of class (12) )

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Mixture A was mixed in different proportions by weight with 2-cyano-6-naphthyl trans-4-n-heptylcyclohexane

-l-carboxylate (compound 12.1), and the table below records measured transition temperatures for those mixtures :

5	Mixture A	Compound 12.1	S <sub>A</sub> -N Transition temperature	N-I Transition temperature
	94%	6%	56.7°	59.8-61.5°
10	90%	10%	58.6°	62.8-64.1°
	85%	15%	60.7°	67.0-68.2°
	80%	20%	63.3°	71.0-72.5°

15 Example 10 (use of a compound of class (13) )

Mixture A was mixed in different proportions by weight with 4-cyano-4'-biphenyl 4-n-octyloxybenzoate (compound 13.1), and the table below records measured transition temperatures for those mixtures :

25	Mixture A	Compound 13.1	S <sub>A</sub> -N Transition temperature	N-I Transition temperature
	97%	3%	56.5-56.9°	59.6-61.4°
	94%	6%	59.4-59.7°	62.2-65.6°
30	91%	9%	61.9-62.2°	66.2-69.8°

Example 11 (use of a compound of class (4) )

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Mixture A was mixed in different proportions by weight with 4-cyanophenyl 4-n-heptylbiphenyl carboxylate



(compound 4.1), and the table below records measured transition temperatures for those mixtures :

5	Mixture A	Compound 4.1	S <sub>A</sub> -N Transition temperature	N-I Transition temperature
	95%	5%	58.5°	60.6-61.0°
10	90%	10%	63.0°	66.5-67.0°
	85%	15%	67.5°	71.6-72.5°

15 Example 12 (use of a compound of class (11) )

Mixture A was mixed in different proportions by weight with 2-cyano-6-naphthyl 4-n-dodecylbenzoate (compound 11.1), and the table below records measured transition  
20 temperatures for those mixtures :

25	Mixture A	Compound 11.1	S <sub>A</sub> -N Transition temperature	N-I Transition temperature
	90%	10%	58.0°	60.8-61.9°
	85%	15%	61.0°	63.9-65.4°

30 Example 13 (use of a compound of class (8) )

Mixture A was mixed in different proportions by weight with 4-cyano-4'-biphenyl trans-4-n-heptylcyclohexyl-  
35 benzoate (compound 8.1), and the table below records measured transition temperatures for those mixtures :

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5	Mixture A	Compound 8.1	S <sub>A</sub> -N Transition temperature	N-I Transition temperature
	99%	1%	55.0°	56.8-59.4°
	98%	2%	57.3°	58.9-62.7°
10	97%	3%	58.1°	59.9-64.3°
	96%	4%	59.3°	62.0-66.4°
	95%	5%	60.8°	63.6-71.5°

15 Example 14 (use of a compound of class (14) )

20 Mixture A was mixed in different proportions by weight with 2-cyano-6-naphthyl 4-n-octyloxybenzoate (compound 14.1), and the table below records measured transition temperatures for those mixtures :

25	Mixture A	Compound 14.1	S <sub>A</sub> -N Transition temperature	N-I Transition temperature
	90%	10%	59.0°	63.8-65.1°
	85%	15%	62.1°	67.7-69.2°

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The following are examples of mixtures containing more than one compound selected from classes 4 to 14 :

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Example 15

5	38.5%	4-Cyano-4'- <u>n</u> -octylbiphenyl
	30.0%	4-Cyano-4'- <u>n</u> -decylbiphenyl
	8.4%	4-Cyano-4'- <u>n</u> -decyloxybiphenyl
	4.1%	4-Cyano-4"- <u>n</u> -nonylterphenyl
10	10.0%	4-Cyano-4'biphenyl <u>trans</u> -4- <u>n</u> -pentyl- cyclohexane-1-carboxylate
	9.0%	4-Cyano-4'-biphenyl <u>trans</u> -4'- <u>n</u> -heptylcyclohexane-1-carboxylate

S<sub>A</sub> -N, 72.4°C: N-I, 78.3-83.2°C.

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Example 16

20	38.9%	4-Cyano-4'- <u>n</u> -octylbiphenyl
	30.3%	4-Cyano-4'- <u>n</u> -decylbiphenyl
	8.6%	4-Cyano-4'- <u>n</u> -decyloxybiphenyl
	4.1%	4-Cyano-4"- <u>n</u> -nonylterphenyl
25	9.1%	4-Cyano-4'-biphenyl <u>trans</u> -4- <u>n</u> - heptylcyclohexane-1-carboxylate
	9.0%	4-Cyano-4'-biphenyl 4- <u>n</u> -decyl- benzoate

S<sub>A</sub> -N, 70.0°C: N-I, 72.8-77.8°C.

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Example 17

5	40.2%	4-Cyano-4'- <u>n</u> -octylbiphenyl
	31.3%	4-Cyano-4'- <u>n</u> -decylbiphenyl
	8.8%	4-Cyano-4'- <u>n</u> -decyloxybiphenyl
	4.3%	4-Cyano-4"- <u>n</u> -nonylterphenyl
10	9.4%	4-Cyano-4'-biphenyl <u>trans</u> -4- <u>n</u> -heptylcyclohexane-1-carboxylate
	6.0%	4-Cyano-4'-biphenyl 4- <u>n</u> -heptyl-biphenyl-4'-carboxylate

S<sub>A</sub> -N, 67.3°C: N-I, 70.7-77.8°C.

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Example 18

20	36.0%	4-Cyano-4'- <u>n</u> -octylbiphenyl
	28.0%	4-Cyano-4'- <u>n</u> -decylbiphenyl
	8.8%	4-Cyano-4'- <u>n</u> -decyloxybiphenyl
	3.8%	4-Cyano-4"- <u>n</u> -nonylterphenyl
25	8.4%	4-Cyano-4'-biphenyl <u>trans</u> -4- <u>n</u> -heptylcyclohexane-1-carboxylate
	10.0%	2-Cyano-6-naphthyl <u>trans</u> -4- <u>n</u> -heptyl-cyclohexane-1-carboxylate
30	6.0%	4-Cyano-4'-biphenyl 4- <u>n</u> -decylbenzoate

S<sub>A</sub> -N, 73.7°C: N-I, 81.4-84.4°C.

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Example 19

5	41.5%	4-Cyano-4'- <u>n</u> -octylbiphenyl
	22.4%	4-Cyano-4'- <u>n</u> -decylbiphenyl
	6.1%	4-Cyano-4'- <u>n</u> -decyloxybiphenyl
10	10.0%	4-Cyano-4'-biphenyl <u>trans</u> -4- <u>n</u> -heptylcyclohexane-1-carboxylate
	10.0%	4-Cyano-4'-biphenyl <u>trans</u> -4- <u>n</u> -pentylcyclohexane-1-carboxylate
	10.0%	2-Cyano-6-naphthyl <u>trans</u> -4- <u>n</u> -heptylcyclohexane-1-carboxylate
15	$S_A$ -N, 71.7°C: N-I, 83.1-87.9°C.	

Example 20

20	42.1%	4-Cyano-4'- <u>n</u> -octylbiphenyl
	22.8%	4-Cyano-4'- <u>n</u> -decylbiphenyl
	6.2%	4-Cyano-4'- <u>n</u> -decyloxybiphenyl
	4.5%	4-Cyano-4'- <u>n</u> -nonylterphenyl
25	8.4%	4-Cyano-4'-biphenyl <u>trans</u> -4- <u>n</u> -heptylcyclohexane-1-carboxylate
	10.0%	2-Cyano-6-naphthyl <u>trans</u> -4- <u>n</u> -heptylcyclohexane-1-carboxylate
30	6.0%	4-Cyanophenyl 4- <u>n</u> -heptylbiphenyl carboxylate
35	$S_A$ -N, 72.2°C: N-I, 81.7-84.2°C.	

Example 21

	36.8%	4-Cyano-4'- <u>n</u> -octylbiphenyl
	28.6%	4-Cyano-4'- <u>n</u> -decylbiphenyl
5	8.1%	4-Cyano-4'- <u>n</u> -decyloxybiphenyl
	3.9%	4-Cyano-4"- <u>n</u> -nonylterphenyl
	8.6%	4-Cyano-4'-biphenyl <u>trans</u> -4- <u>n</u> -heptylcyclohexane-1-carboxylate
10	10.0%	2-Cyano-6-naphthyl <u>trans</u> -4- <u>n</u> -heptylcyclohexane-1-carboxylate
	4.0%	4-Cyano-4'-biphenyl 4- <u>n</u> -heptylbiphenyl-4'-carboxylate
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S<sub>A</sub> -N, 73.9°C: n-I, 81.7-87.6°C.

Example 22

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This example illustrates the increasing depression of the onset of melting with increasing complexity of the mixture. In this example the following abbreviations are used:

25

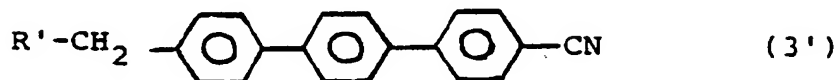
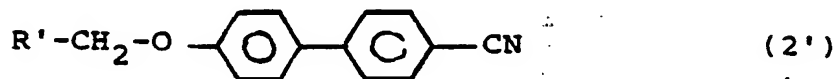
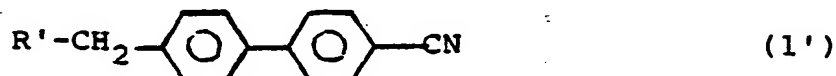
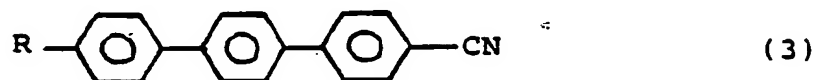
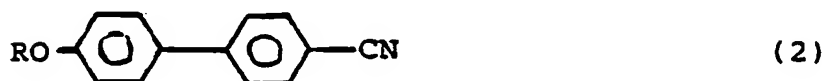
	K24	4-Cyano-4'- <u>n</u> -octylbiphenyl
	K30	4-Cyano-4'- <u>n</u> -decylbiphenyl
	M30	4-Cyano-4'- <u>n</u> -decyloxybiphenyl
	T27	4-Cyano-4"- <u>n</u> -nonylterphenyl
30	C12E	4-Cyano-4'-biphenyl 4- <u>n</u> -decylbenzoate
	7-NAP	2-Cyano-6-naphthyl <u>trans</u> -4- <u>n</u> -heptylcyclohexane-1-carboxylate
	7-CHE	4-Cyano-4'-biphenyl <u>trans</u> -4- <u>n</u> -heptylcyclohexane-1-carboxylate
35	BB21	4-Cyano-4'-biphenyl 4- <u>n</u> -heptylbiphenyl-4'-carboxylate

Example 22 - Table  
Composition by % weight

K24	65.4	59.9	60.3	60.5	55.1	55.2	55.0
K30	22.6	19.8	19.2	19.2	16.1	16.0	16.2
M30	12.0	10.2	10.3	10.2	8.5	8.5	8.3
T27		10.1			10.3	10.4	
Cl2E					5.0	4.9	5.2
7-NAP			10.2		5.0		5.1
7-CHE				10.1		5.0	5.1
BB21							5.1
Onset of melting	-1.2°	-6.7°	-5.3°	-6.9°	-10.3°	-14.4°	-17.2°
SA-N Transistion Temperature	45.5°	57.9°	49.8°	58.3°	66.0°	69.3°	64.7°
N-I Transistion temperature	48.2-48.3°	62.1-64.7°	56.1-56.9°	61.1-64.4°	72.0-74.7°	73.3-79.0°	74.5-80.0°

CLAIMS:-

1. A liquid crystal composition exhibiting a smectic A phase comprising as a first part between 40 and 99 % by weight in aggregate of one or more materials selected from one or more of the following six compound classes,

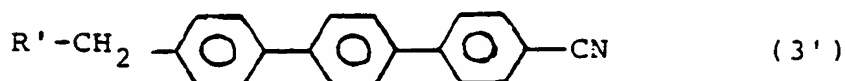
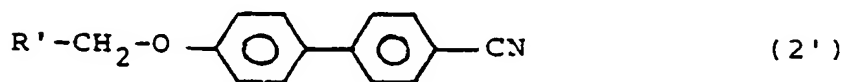
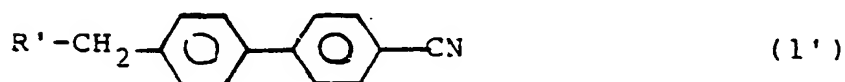
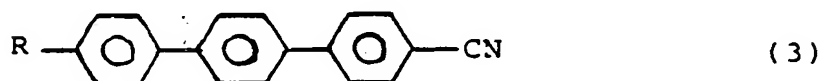
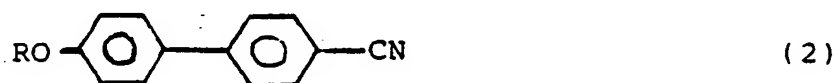
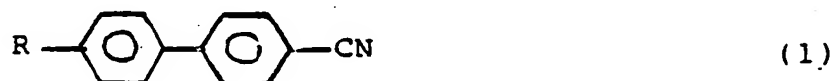


wherein R is in every instance an alkyl chain containing between 2 and 18 carbon atoms and R' is in every instance an alkyl chain containing between 1 and 17 carbon atoms, wherein one or more non-adjacent CH<sub>2</sub>-groups are replaced by oxygen atoms,

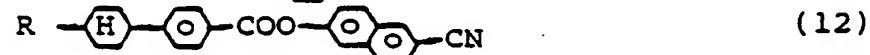
and as a second part between 1 and 60 % by weight of one or more materials of high birefringence and high positive dielectric anisotropy which raise the S<sub>A</sub>-N transition temperature.



2. A liquid crystal composition according to Claim 1, which composition either consists exclusively of a base mixture or consists of a base mixture together with not more than 10 % by weight in aggregate of one or more other constituents, characterised in that the base mixture contains, as a first part, between 40 and 90% by weight in aggregate of one or more materials selected from one or more of the following six compounds classes,



and in that the balance of the base mixture is provided by a second part consisting of one or more materials selected from one or more of the following eleven compound classes,



wherein R is in every instance an alkyl chain containing between 2 and 18 carbon atoms and R' is in every instance an alkyl chain containing between 1 and 17 carbon atoms, wherein one or more non-adjacent CH<sub>2</sub>-groups are replaced by oxygen atoms.

3. A liquid crystal composition as claimed in claim 1 or 2, wherein R is in every instance a straight alkyl chain.
4. A liquid crystal composition as claimed in claim 2 or 3, wherein said other constituent(s) consist of chiral, ionic, surfactant, and/or guest dye additives.
5. A liquid crystal cell filled with a composition as claimed in claim 1, 2, 3 or 4.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 85/00731

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>4</sup> :     C 03 K 19/44; C 09 K 19/46																							
<b>II. FIELDS SEARCHED</b> <div style="text-align: right; font-size: small;">Minimum Documentation Searched *</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 20%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; vertical-align: top;">IPC<sup>4</sup></td> <td style="border: none; vertical-align: top;">C 09 K</td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *</div>			Classification System	Classification Symbols	IPC <sup>4</sup>	C 09 K																	
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IPC <sup>4</sup>	C 09 K																						
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT *</b> <table border="1" style="width: 100%; border-collapse: collapse; font-size: small;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 60%;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 30%;">Relevant to Claim No. <sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">EP, A, 0008956 (U.K. SECRETARY OF STATE DEFENSE) 19 March 1980, see page 3, lines 1-23; page 8, example 1; page 9, examples 2,3,4; page 10, examples 5-7; page 11, example 8; page 12, example 21; page 15, example 33; page 25, lines 1-17</td> <td style="text-align: center; vertical-align: top;">1-5</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="text-align: center; vertical-align: top;">--</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">FR, A, 2407973 (U.K. SECRETARY OF STATE DEFENCE) 1 June 1979, see page 2, lines 7-27; page 7; page 8; page 9, lines 1-11; claims 1,4,6,8,10</td> <td style="text-align: center; vertical-align: top;">1-5</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="text-align: center; vertical-align: top;">--</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">EP, A, 0044646 (CHISSO) 27 January 1982, see page 2, lines 1-25; examples 6,7; claims 1-7</td> <td style="text-align: center; vertical-align: top;">1-5</td> </tr> <tr> <td colspan="3" style="text-align: center; padding-top: 20px;">-----</td> </tr> </tbody> </table>			Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	X	EP, A, 0008956 (U.K. SECRETARY OF STATE DEFENSE) 19 March 1980, see page 3, lines 1-23; page 8, example 1; page 9, examples 2,3,4; page 10, examples 5-7; page 11, example 8; page 12, example 21; page 15, example 33; page 25, lines 1-17	1-5	X	--		X	FR, A, 2407973 (U.K. SECRETARY OF STATE DEFENCE) 1 June 1979, see page 2, lines 7-27; page 7; page 8; page 9, lines 1-11; claims 1,4,6,8,10	1-5	X	--		X	EP, A, 0044646 (CHISSO) 27 January 1982, see page 2, lines 1-25; examples 6,7; claims 1-7	1-5	-----		
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X	EP, A, 0044646 (CHISSO) 27 January 1982, see page 2, lines 1-25; examples 6,7; claims 1-7	1-5																					
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"G" document member of the same patent family</p> </div> </div>																							
<b>IV. CERTIFICATION</b> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;">           Date of the Actual Completion of the International Search  <div style="text-align: center;">25th March 1986</div> </td> <td style="width: 50%; border: none; vertical-align: top;">           Date of Mailing of this International Search Report  <div style="text-align: center;">14 APR 1986</div> </td> </tr> <tr> <td style="border: none; vertical-align: top;">           International Searching Authority  <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="border: none; vertical-align: top;">           Signature of Authorized Officer  <div style="text-align: center;">M. VAN MOL </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">25th March 1986</div>	Date of Mailing of this International Search Report <div style="text-align: center;">14 APR 1986</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">M. VAN MOL </div>																	
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/EP 85/00731 (SA 11858)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 04/04/86.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0008956	19/03/80	GB-A,B 2031010 US-A- 4462924	16/04/80 31/07/84
FR-A- 2407973	01/06/79	GB-A,B 2009219 DE-A- 2847601 JP-A- 54075484 US-A- 4227778 CH-A- 638827	13/06/79 03/05/79 16/06/79 14/10/80 14/10/83
EP-A- 0044646	27/01/82	JP-A- 57021359 US-A- 4387038	04/02/82 07/06/83